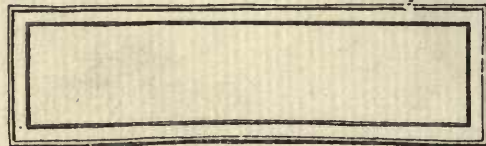
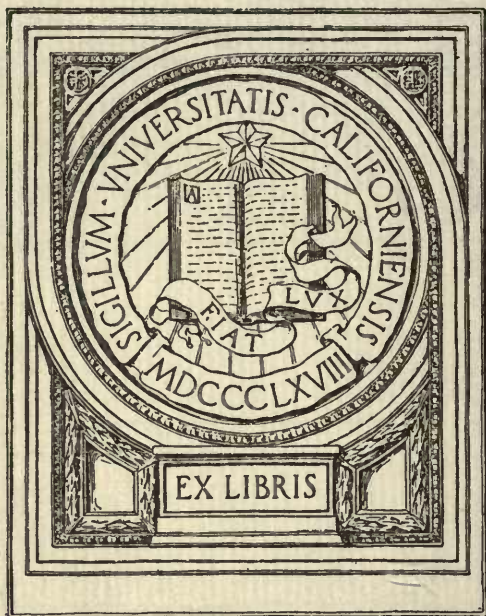
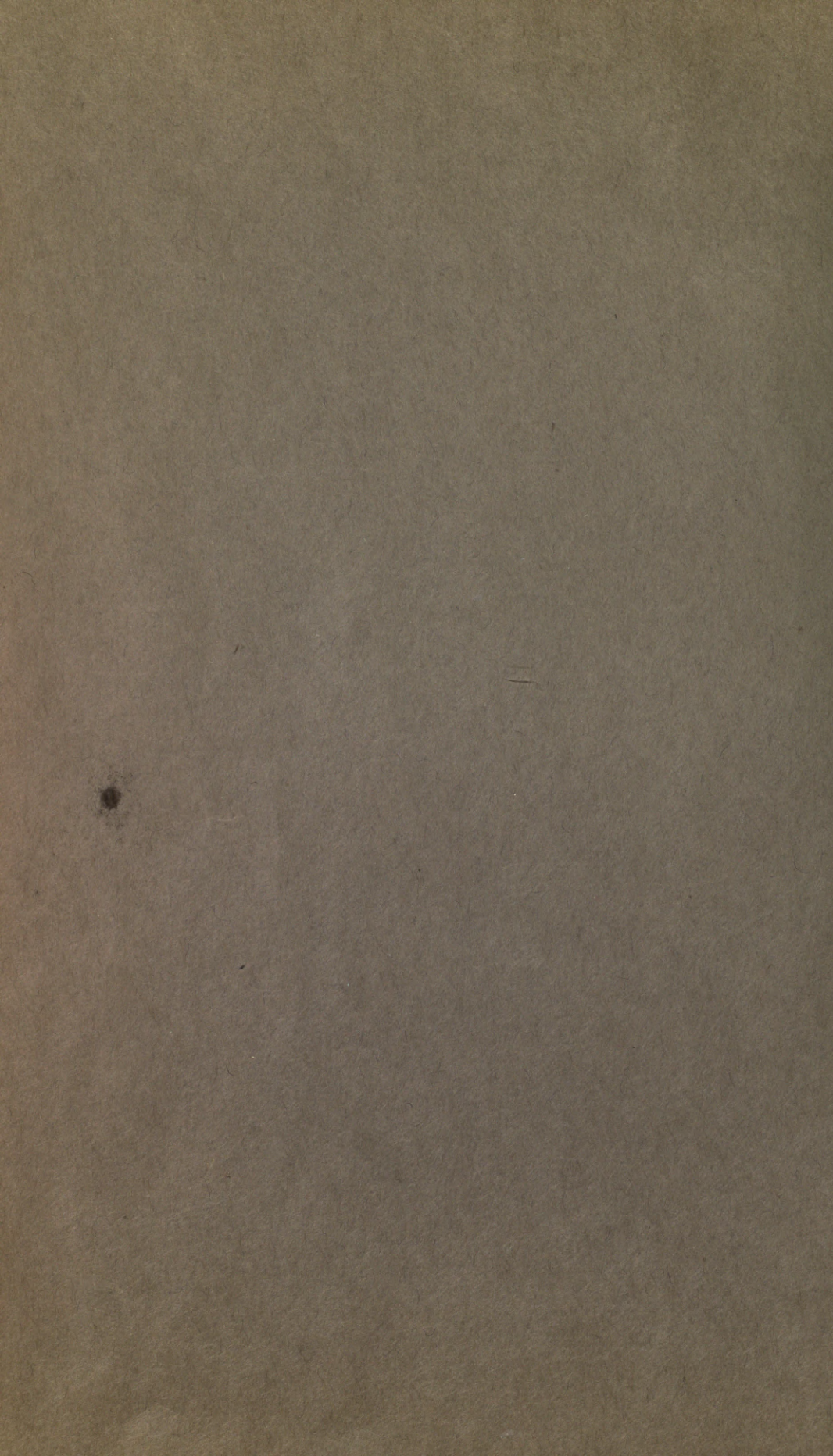


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A Ph. D. Thesis by
Thomas Erwin Phipps

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THE CONDUCTANCE OF CERTAIN ALKALI METALS IN LIQUID

AMMONIA AND IN METHYLAMINE

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The photometric investigation by Gibson and Argo¹ of the blue solutions of several alkali and alkaline earth metals in liquid ammonia and in methylamine led to identical absorption curves in liquid ammonia, but to more complex ones in methylamine. The hypothesis was advanced that in liquid ammonia the dissociation of the metal into electrons is nearly complete, and that the solvation of these electrons is nearly complete; whereas in methylamine the concentration of the unionized metal is considerable, and the solvation of the electrons is incomplete. The most promising method of studying the interesting questions of ionization and solvation appeared to be in determining the temperature coefficients of conductivity of the blue solutions in liquid ammonia and in methylamine .

Since liquid ammonia was more available than methylamine, it was used as solvent in all earlier experiments, and later when the manipulation was well established, solutions in methylamine were studied. While the investigation was in progress, the recent comprehensive study by Kraus² of conductances in liquid ammonia was published, and his results are confirmed at several points by our own.

¹ Gibson and Argo, Phys. Rev., 1, 33 (1916);
This Journal, 40, 1327 (1916).

² Kraus, This Journal, 43, 749 (1921).

James G. Thompson
of M. D. Thesis by

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AMMONIA AND IN METHYLAMINE

Deposited in the Library of the U.S. National Bureau of Standards
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the blue solutions of several alkali and alkaline earth metals in liquid ammonia and in methylamine led to identical absorption curves in liquid ammonia, but to more complex ones in methylamine. The hypothesis was advanced that in liquid ammonia the dissociation of the metal into electrons is nearly complete, and that the solvation of these electrons is nearly complete; whereas in methylamine the concentration of the ionized metal is considerable, and the solvation of the electrons is incomplete. The most promising method of studying the interesting questions of ionization and solvation appeared to be in determining the temperature coefficients of conductivity of the blue solutions in liquid ammonia and in methylamine.

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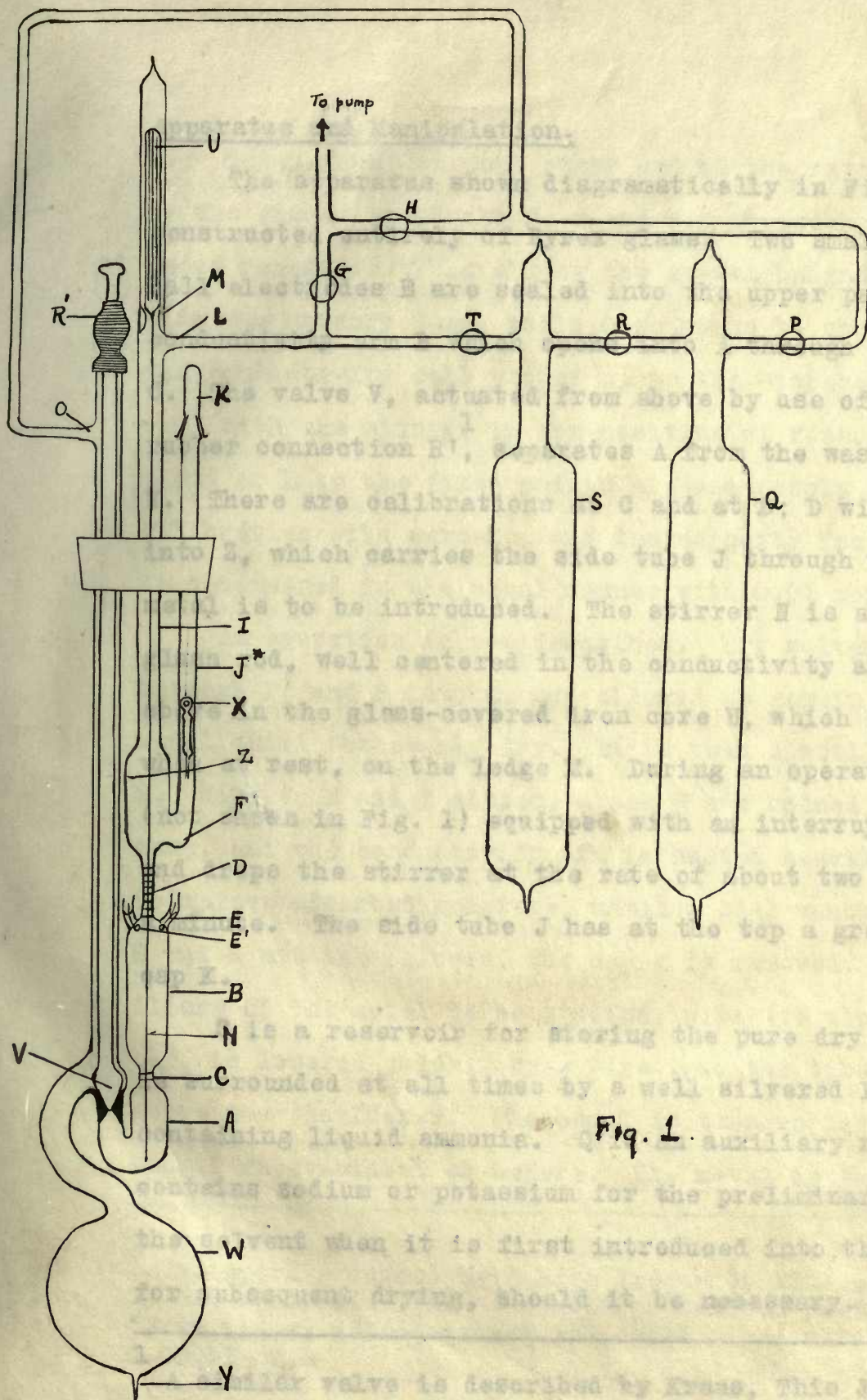


Fig. 1

* The side-tube J enters Z at a point higher than that shown in the figure.

Apparatus and Manipulation.

The apparatus shown diagrammatically in Fig. 1 is constructed entirely of Pyrex glass. Two small platinum ball electrodes E are sealed into the upper part of the conductivity arm B which opens into A through a constriction C. The valve V, actuated from above by use of the taut rubber connection R¹, separates A from the waste reservoir W. There are calibrations at C and at D; D widens above into Z, which carries the side tube J through which the metal is to be introduced. The stirrer N is a very slender glass rod, well centered in the conductivity arm, terminating above in the glass-covered iron core U, which is supported, when at rest, on the ledge M. During an operation, a solenoid (not shown in Fig. 1) equipped with an interruptor lifts and drops the stirrer at the rate of about two hundred times a minute. The side tube J has at the top a ground glass cap K.

S is a reservoir for storing the pure dry solvent, and is surrounded at all times by a well silvered Dewar vessel containing liquid ammonia. Q is an auxiliary reservoir which contains sodium or potassium for the preliminary drying of the solvent when it is first introduced into the system, and for subsequent drying, should it be necessary. S and Q are

1 00001 mm.

A similar valve is described by Kraus, This Journal, 36, 866(

Apparatus and Manipulation.

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made independent of each other and of the rest of the system by the vacuum stopcocks T, r and P. Stopcock H connects the waste reservoir W and all of the system behind the valve V with the mercury pump, while G connects to the pump all of the conductivity cell proper up to the stopcock T.

With the stirrer in its position of rest, the volumes of A and of B to the fixed points are accurately determined by calibration with mercury, and the capacity factor of the cell is determined in the usual manner with 0.01 normal KCl.

An operation is now described. Dry solvent is distilled through P' and P into Q, and allowed to remain there on the metal until thoroughly dry. It is then distilled into S through R. With P, R and T closed, G and H are opened to the mercury pump, and the conductivity arm is heated heavily with a flame to remove adsorbed moisture, until a high vacuum is obtained.¹ G and H are then closed, the cap K is removed, and a capillary of the metal to be studied, with its tip freshly broken off, is lowered quickly by a wire into the tube J to a point above the shoulder F. The cap K is then replaced and the vessel re-evacuated as before. The metal is then melted out

¹ The regulation is very accurate. The bath is then replaced

The spark produced by a high frequency 110v coil was entirely extinguished. When a similar condition prevailed in other Pyrex lines, McLeod gauges indicated a pressure of less than 0.00001 mm.

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of the capillary by gentle heating of J, and rests as a bright globule in F, whence by further heating it is distilled, in whole or in part as desired, into the wider tube Z where it appears as a bright mirror on the walls of the glass. Potassium and caesium distill very rapidly, and even sodium distills quite readily in a very high vacuum. The slight amount of oxide which accompanied the introduction of the capillary remains in F throughout the run, and solvent is never condensed on it.

G and H are then closed, and the conductivity cell is surrounded by a bath of boiling liquid ammonia with its level at Z. Dry solvent is then distilled through T from the reservoir S, and the metal is completely washed down into A and B until the blue solution fills the vessel from the valve up to a point in D. Stirring is continued till the conductivity reaches a constant value, when the volume is read with the stirrer at rest.

To make a dilution, the bath is lowered away for a moment till its level is at C, and the valve is slightly unseated by upward tension at R' until the level of the blue solution has fallen to C. With a well ground valve this regulation is very accurate. The bath is then replaced and fresh solvent distilled in as before, with the stirrer

1 Alcohol was not used on account of the uncertainty of the end-point when it was present.

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To make a dilution, the bath is lowered away for a moment till its level is at G, and the valve is slightly unseated by upward tension at R, until the level of the blue solution has fallen to G. With a well ground valve this regulation is very accurate. The bath is then replaced and fresh solvent distilled in as before, with the stirrer

operating all the while. At the end of a run, which rarely required more than two hours, stopcocks H, P and R are opened and the solvent is returned by distillation from the blue solution in W to S, leaving in W all the metal which was originally present in the first solution. With the solvent isolated in S, the last trace of solvent is removed from the metal by evacuation and by slight warming of W.

The tip Y is then broken, and the metal is oxidized by a stream of moist air admitted at P'. W is then washed out thoroughly, the solution is evaporated to a small volume to remove ammonia, and the solution is titrated with 0.1 normal HCl, with methyl orange as an indicator.¹ All necessary data are now at hand for the calculation of volume-normal concentrations and specific and molecular conductivities.

To prepare the vessel for another run, the empty capillary X is withdrawn and the vessel filled through J down as far as the valve with cleaning mixture, which is then heated and allowed to stand in the vessel for several minutes. It is forced out by way of V through Y, and followed by many changes of distilled water, which is removed in the same way. Finally, with the valve clamped open, the vessel is dried thoroughly by a stream of warm air coming from P' and from K. The tips

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point when it was present.

Results.
nation proceeds as before.

The filling of capillaries is as follows: tubing of small bore is constricted further, and bent at about a 60° angle at the constriction. One end of the tube is sealed off at a suitable distance from the bend, and the other end is sealed to a vacuum line. After being evacuated, the tube is sealed off at a point which leaves a symmetrical V-shape. The tip of the "V" is put below the surface of a globule of the molten metal and broken; this leaves the two tubes terminating in small capillaries entirely filled with bright clean metal. To prevent further oxidation of the metal at the tips, the capillaries are kept under oil.

The two temperatures employed in most of the experiments were the boiling point of liquid ammonia, and a temperature about 15° lower (-48.5°C), obtained by bubbling dried air at a controlled rate through the bath. By hand regulation the temperature was kept constant within 0.1°C or 0.2°C . Chloroform, frozen by means of solid carbon dioxide was used as a bath in two or three of the experiments, but its temperature was found to be quite inconstant, and because of the difficulty of making a satisfactory constant temperature bath in the neighborhood of -70.0°C ., work at the lower temperature was abandoned, although on account of slower fading it seemed desirable to work at that temperature.

By "fading" is meant the reaction of the metal with the solvent to form the metal amide.

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-33.5° C.

Results.

The work in liquid ammonia comprised measurements at three temperatures, -33.5°C , -48.5°C , and -70.0°C . of the conductivities of the blue solutions of sodium between concentrations of 0.4 normal and 0.0001 normal, and measurements at the first two temperatures of potassium solutions. Curves I, II and III of Fig. 2 show the specific conductance as a function of the "dilution" V , and Curves I', II' and III' show the molecular conductivity Λ as a function of V . The agreement between the different runs is good as far as 0.001 normal, but beyond that concentration the "fading"¹ is appreciable and erratic. At -33.5°C . the highest value for $\log k$ at $\log V = 4.0$ (0.0001 normal) corresponded to a molecular conductivity of 970, which is lower than the best value of Kraus,¹ - about 1000 at this dilution.

Since the concentrations dealt with here are volume-normal, whereas Kraus's concentrations were weight normal, a direct comparison of the two would involve a knowledge of the densities; or assuming the accuracy of the two sets of data, the densities could be calculated. Unfortunately our measurements do not extend into the most concentrated blue solutions where the densities are most abnormal. A careful comparison of two representative series obtained by

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² Loc. cit.

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1 By "leading" is meant the reaction of the metal with the solvent to form the metal amide.

Table I

Conductance of Sodium in Liquid Ammonia

 -33.5°C.

Series I				Series II			
No.	log k	log V	Λ	No.	log k	log V	Λ
1	0.198	0.111	2038	1	2.978	0.793	591
2	1.490	0.406	787	2	2.431	1.237	466
3	1.074	0.696	587	3	2.019	1.680	501
4	2.710	0.985	495	4	3.662	2.125	613
5	2.387	1.277	461	5	3.301	2.569	742
6	2.116	1.561	475	6	4.882	3.013	786
7	3.877	1.844	526				
8	3.657	2.125	605				
9	3.422	2.419	693				
10	3.172	2.708	759				
11	4.907	2.996	799				
12	4.633	3.283	825				
13	4.354	3.576	852				

Series III				Series IV			
No.	log k	log V	Λ	No.	log k	log V	Λ
1	2.896	0.849	556	1	2.585	1.087	470
2	2.382	1.295	476	2	2.138	1.530	466
3	3.975	1.739	518	3	3.772	1.973	556
4	3.625	2.182	642	4	3.418	2.416	683
5	3.260	2.625	769	5	3.025	2.859	766
6	4.834	3.068	798	6	4.592	3.302	780
7	4.329	3.511	692	7	4.084	3.745	675

 -48.5°C.

Series V				Series VI			
No.	log k	log V	Λ	No.	log k	log V	Λ
1	1.062	0.641	505	1	1.200	0.536	545
2	2.500	1.086	386	2	2.616	0.981	396
3	2.023	1.531	358	3	2.120	1.423	349
4	3.630	1.984	412	4	3.715	1.873	388
5	3.282	2.427	512	5	3.359	2.322	480
6	4.910	2.870	603	6	4.975	2.765	550
7	4.472	3.320	620				

Table I
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-33.5°C.

Series I				Series II			
No.	log K	log V	Λ	No.	log K	log V	Λ
1	0.198	0.117	5038	1	2.978	0.793	591
2	1.490	0.408	787	2	2.647	1.237	468
3	1.074	0.636	587	3	2.079	1.680	801
4	1.710	0.985	425	4	2.125	2.125	613
5	1.387	1.277	461	5	2.301	2.569	748
6	1.561	1.561	475	6	4.882	3.013	786
7	1.844	1.844	526				
8	2.125	2.125	605				
9	2.419	2.419	693				
10	2.708	2.708	789				
11	2.995	2.995	799				
12	3.283	3.283	825				
13	3.576	3.576	853				

Series III				Series IV			
No.	log K	log V	Λ	No.	log K	log V	Λ
1	2.896	0.849	556	1	2.585	1.087	470
2	2.383	1.295	476	2	2.138	1.530	466
3	1.975	1.739	619	3	1.773	1.973	556
4	1.623	2.182	678	4	2.418	2.418	683
5	1.260	2.625	769	5	2.025	2.869	766
6	1.834	3.068	798	6	4.592	3.302	790
7	4.329	3.511	692	7	4.084	3.745	676

Series V				Series VI			
No.	log K	log V	Λ	No.	log K	log V	Λ
1	1.062	0.641	508	1	1.200	0.538	545
2	1.500	1.066	386	2	2.616	0.981	396
3	1.023	1.531	358	3	1.710	1.423	549
4	1.630	1.984	412	4	2.715	1.873	398
5	2.282	2.427	512	5	2.329	2.322	460
6	2.910	2.870	603	6	4.976	2.765	550
7	4.473	3.320	520				

-48.5°C.

Table I (concluded)

-48.5° C.

Series VII

No.	log k	log V	Δ
1	<u>2</u> .850	0.804	451
2	<u>2</u> .310	1.248	361
3	<u>3</u> .872	1.694	368
4	<u>3</u> .508	2.139	444
5	<u>3</u> .156	2.584	550
6	4.728	3.028	570

-70.0° C.

Series VIII

No.	log k	log V	Δ
1	<u>2</u> .836	0.654	309
2	<u>2</u> .436	0.971	256
3	<u>2</u> .056	1.302	228
4	<u>3</u> .723	1.636	229
5	<u>3</u> .448	1.963	257
6	<u>3</u> .168	2.294	290
7	4.896	2.615	324
8	4.611	2.935	351
9	4.321	3.256	360

Series IX

No.	log k	log V	Δ
1	<u>1</u> .295	0.310	403
2	<u>2</u> .679	0.778	287
3	<u>2</u> .121	1.238	229
4	<u>3</u> .657	1.700	228
5	<u>3</u> .289	2.162	283
6	<u>4</u> .933	2.625	362
7	4.547	3.092	436

Table I (continued)

-48.5° C.

Series VII

No.	log K	log V	Δ
1	1.850	0.804	451
2	1.810	1.848	351
3	1.818	1.834	368
4	1.808	2.139	444
5	1.756	2.584	350
6	1.728	2.028	570

-40.0° C.

Series VIII

No.	log K	log V	Δ	No.	log K	log V	Δ
1	1.836	0.654	309	1	1.835	0.310	408
2	1.818	0.871	258	2	1.879	0.778	287
3	1.808	1.808	338	3	1.811	1.838	329
4	1.828	1.828	339	4	1.857	1.700	338
5	1.868	1.868	297	5	1.889	2.162	283
6	1.894	2.294	330	6	1.833	2.625	262
7	1.816	2.616	334	7	1.847	3.092	426
8	1.811	2.935	331				
9	1.821	3.256	360				

Series IX

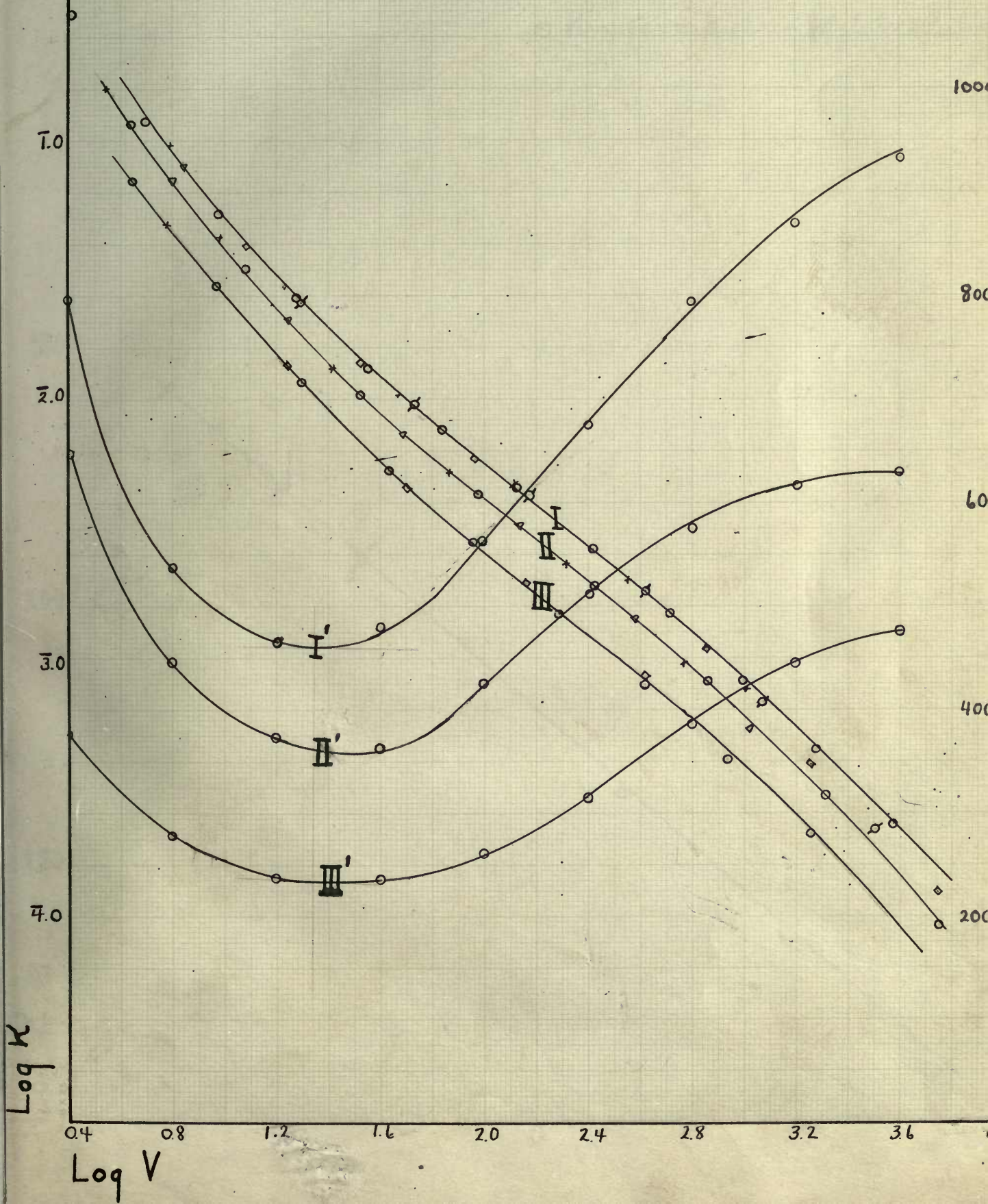
No.	log K	log V	Δ
1	1.835	0.310	408
2	1.879	0.778	287
3	1.811	1.838	329
4	1.857	1.700	338
5	1.889	2.162	283
6	1.833	2.625	262
7	1.847	3.092	426

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Fig 2.

Na in NH_3

I - -33.5°C ; II - -48.5°C ; III - -70.0°C .



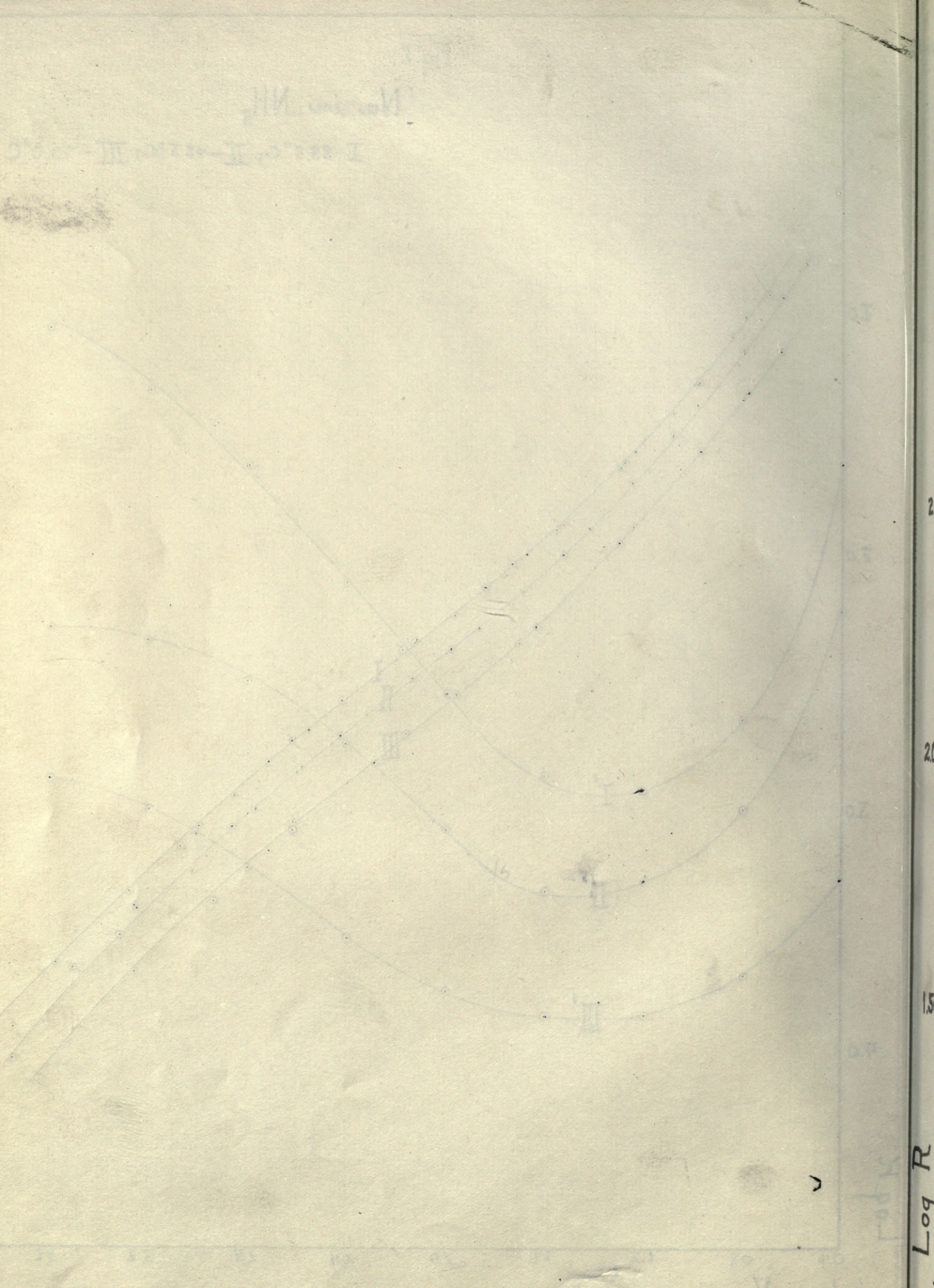
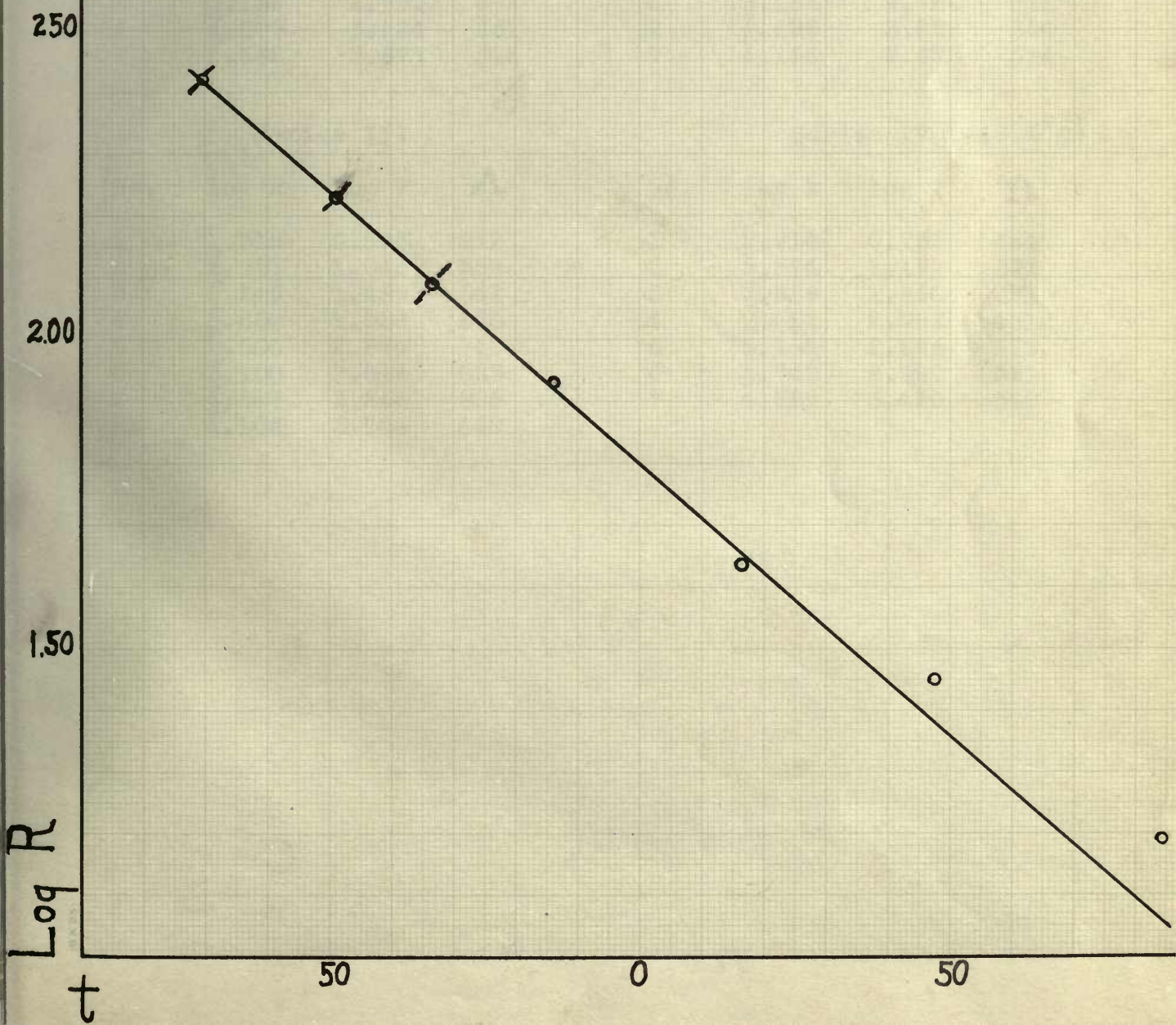


Fig. 3

Na in NH_3

⊗ Values at 0.004 normal

○ Kraus's values in "dilute solution"





Λ in NH_3
 I-33.5°C.; II-48.5°C.

Table II

Conductance of Potassium in Liquid Ammonia

Series I				Series II			
No.	log k	log V	Λ	No.	log k	log V	Λ
1	$\bar{2}.766$	1.015	604	1	$\bar{2}.774$	1.015	615
2	$\bar{2}.283$	1.460	554	2	$\bar{2}.292$	1.458	563
3	$\bar{3}.889$	1.903	620	3	$\bar{3}.897$	1.901	628
4	$\bar{3}.526$	2.346	746	4	$\bar{3}.542$	2.344	769
5	$\bar{3}.135$	2.790	842	5	$\bar{3}.154$	2.786	871
6	$\bar{4}.579$	3.234	651	6	$\bar{4}.698$	3.228	844
7	$\bar{5}.862$	3.677	346	7	$\bar{4}.168$	3.673	694

Series III				Series IV (-48.5°C)			
No.	log k	log V	Λ	No.	log k	log V	Λ
1	$\bar{1}.315$	0.595	813	1	$\bar{2}.914$	0.752	464
2	$\bar{2}.731$	1.045	598	2	$\bar{2}.374$	1.197	373
3	$\bar{2}.245$	1.489	542	3	$\bar{3}.929$	1.640	371
4	$\bar{3}.860$	1.932	620	4	$\bar{3}.552$	2.082	431
5	$\bar{3}.500$	2.374	749	5	$\bar{3}.185$	2.524	512
6	$\bar{3}.100$	2.815	823	6	$\bar{4}.749$	2.967	521
7	$\bar{4}.647$	3.258	805	7	$\bar{4}.329$	3.410	549
8	$\bar{4}.103$	3.703	640				

Table II

Conductance of Potassium in Liquid Ammonia

Series I

No.	log K	log V	Δ
1	1.766	1.015	604
2	1.883	1.460	554
3	1.883	1.903	620
4	1.883	2.346	746
5	1.135	2.790	843
6	1.573	3.234	651
7	1.863	3.677	346

Series II

No.	log K	log V	Δ
1	1.774	1.015	615
2	1.892	1.458	563
3	1.897	1.901	628
4	1.843	2.344	769
5	1.134	2.786	871
6	1.693	3.228	844
7	1.168	3.673	694

Series III

No.	log K	log V	Δ
1	1.315	0.553	813
2	1.731	1.045	598
3	1.245	1.489	543
4	1.860	1.932	680
5	1.500	2.374	749
6	1.100	2.815	853
7	1.647	3.258	805
8	1.103	3.703	640

Series IV (-48.5°)

No.	log K	log V	Δ
1	1.914	0.752	464
2	1.374	1.197	373
3	1.929	1.640	371
4	1.552	2.082	431
5	1.166	2.524	512
6	1.149	2.967	521
7	1.329	3.410	545

Fig. 4.

K in NH₃

I-33.5°C. ; II-48.5°C.

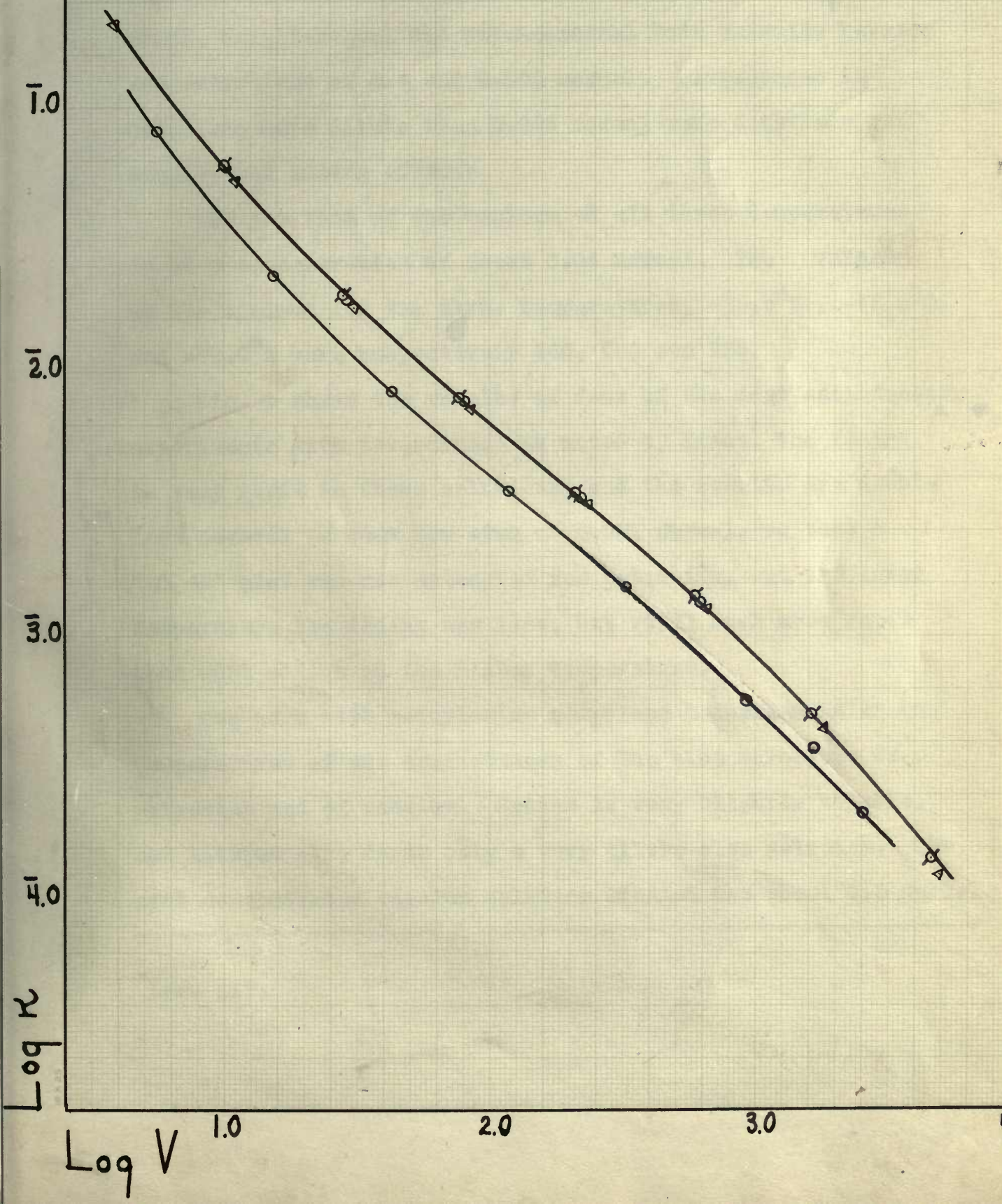


Table III

the two methods showed that within the limits of experimental error, weight-normal and volume-normal data coincide between concentrations of 0.4 and 0.005 normal. Divergences in solutions more dilute than 0.005 normal were doubtless not density but fading effects.

The position of the minimum at all three temperatures is at a concentration of about 0.04 normal. The values at the minimum for the three temperatures, $-33.5^{\circ}\text{C}.$, $-48.5^{\circ}\text{C}.$ and -70.0°C were respectively 460, 360 and 235.

Fig. 4 shows the results of four of the most satisfactory experiments with potassium. As noted by Kraus, the fading is very rapid in these solutions, and the results are doubtless several percent low even at 0.001 normal, so that a " Λ -k" plot was not attempted for potassium. At the lower temperature the fading was less, but still much more rapid than with sodium at the higher temperature.

The work with methylamine comprised measurements at two temperatures of the conductances of the blue solutions of potassium and of caesium. Sodium is very slightly soluble, and lithium also forms only a very dilute blue solution. The most concentrated caesium solution studied was about 0.3 normal.

1
Loc. cit.

The two methods showed that within the limits of experimental error, weight-normal and volume-normal data coincide between concentrations of 0.4 and 0.005 normal. Divergence in solutions more dilute than 0.005 normal were doubtless not merely but being effects.

The position of the minimum at all three temperatures is at a concentration of about 0.04 normal. The values at the minimum for the three temperatures, -33.5°C , -43.5°C , and -70.0°C were respectively 460, 360 and 338.

Fig. 4 shows the results of four of the most satisfactory experiments with potassium. As noted by Kline, the fading is very rapid in these solutions, and the results are doubtless several percent low even at 0.001 normal, so that a "A-X" plot was not attempted for potassium. At the lower temperature the fading was less, but still much more rapid than with sodium at the higher temperature.

The work with potassium comprised measurements at two temperatures of the conductances of the five solutions of potassium and of sodium. Sodium is very slightly soluble, and lithium also forms only a very dilute fine solution. The most concentrated sodium solution studied was about 0.3 normal.

Table III

Conductance of Caesium and of Caesium Iodide in
Methylamine.Series -33.5⁰ C. (Caesium Iodide)

Series I				Series II			
No.	log k	log V	Λ	No.	log k	log V	Λ
1	3.556	1.145	50.3	11	2.302	0.527	167.5
2	3.160	1.591	56.4	2	3.707	0.985	149.9
3	4.839	2.035	74.9	3	3.273	1.453	153.3
4	4.529	2.476	101.2	4	4.926	1.911	168.8
	5.432	3.091	133.8	5	5.584	2.088	22.3

Series III

No.	log k	log V	Λ
1	3.048	1.728	59.7
2	4.740	2.171	81.5
3	4.418	2.620	109.2
4	4.087	3.061	140.7
5	5.703	3.503	159.6

-48.5⁰ C.

Series IV				Series V			
No.	log k	log V	Λ	No.	log k	log V	Λ
1	3.850	0.708	36.1	1	3.691	0.880	37.3
2	3.362	1.163	33.5	2	3.233	1.325	36.2
3	3.005	1.606	40.9	3	4.897	1.768	46.3
4	4.695	2.049	55.5	4	4.577	2.212	61.6
5	4.386	2.492	75.5	5	4.257	2.653	81.3

Series VI

No.	log k	log V	Λ
1	4.588	2.233	66.3
2	4.302	2.678	95.5
3	5.972	3.125	125.1
4	5.612	3.569	151.8
5	5.187	4.011	157.8

Table III

Conductance of Cesium and of Cesium Iodide in
Methylamine.

-33.5°C.

Series II

No.	log K	log V	Δ
1	2.526	1.145	50.8
2	2.160	1.591	55.4
3	4.939	2.035	74.9
4	4.529	2.476	101.2

Series III

No.	log K	log V	Δ
1	3.048	1.788	59.7
2	4.740	2.171	81.5
3	4.418	2.620	109.2
4	4.087	3.061	140.7
5	5.703	3.503	159.6

-48.5°C.

Series V

No.	log K	log V	Δ
1	2.850	0.708	39.1
2	2.362	1.162	33.5
3	3.005	1.606	40.9
4	4.995	2.049	55.5
5	4.388	2.492	76.2

Series VI

No.	log K	log V	Δ
1	4.588	2.832	66.2
2	4.302	2.678	95.2
3	3.972	2.122	125.1
4	3.612	2.569	151.8
5	3.187	4.011	157.8

Cs in CH₃NH₂

I - 33.5°C., II - 48.5°C.

Table III (concluded)

Series VII (Caesium Iodide)

-33.5°C				-48.5°C.			
No.	log k	log V	Δ	No.	log k	log V	Δ
1	4.797	1.296	12.4	1	4.747	1.288	10.8
2	4.370	1.744	13.0	2	4.326	1.736	11.5
3	4.022	2.193	16.4	3	5.978	2.185	14.6
4	5.708	2.642	22.4	4	5.670	2.634	20.1
5	5.430	3.091	33.2	5	5.384	3.083	29.3

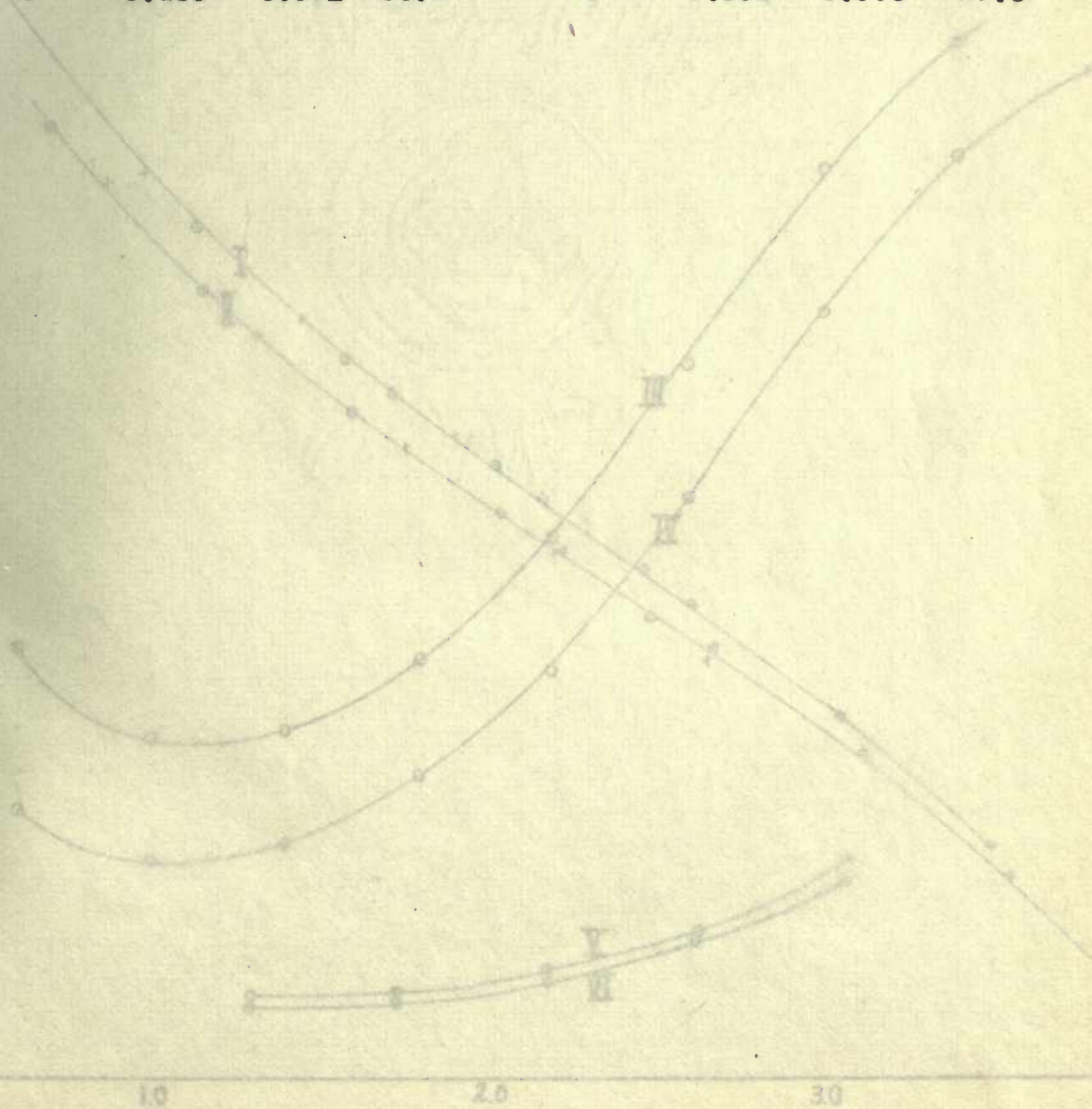


Table III (continued)

Series VII (Oreum Iodide)

-48.5° C.

-32.5° C.

No.	log k	log V	Δ	No.	log k	log V	Δ
1	4.797	1.396	12.4	1	4.747	1.388	10.8
2	4.370	1.744	18.0	2	4.386	1.736	11.5
3	4.022	2.193	16.4	3	3.978	2.185	14.6
4	3.708	2.642	22.4	4	3.670	2.634	20.1
5	3.430	3.091	22.2	5	3.384	3.082	22.8

Fig. 5.

C_s in CH_3NH_2

I - $33.5^\circ C.$; II - $48.5^\circ C.$

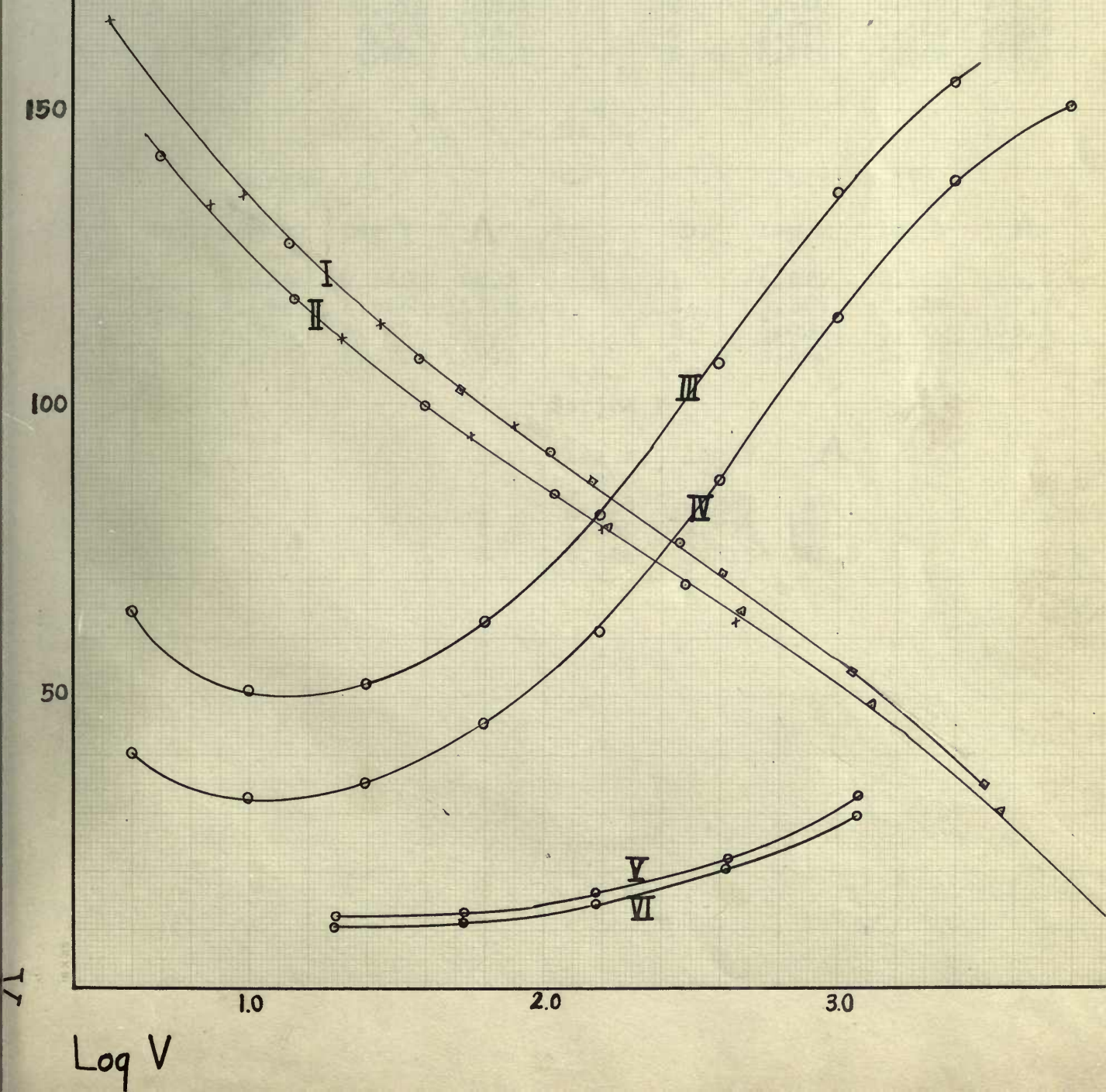


Fig. 2

K in CH_3NH_2

I -33.5°C

II -48.5°C

Table IV

Conductance of Potassium in Methylamine

-48.5°C.

Series I				Series II			
No.	log k	log V	Λ	No.	log k	log V	Λ
1	$\bar{4}.394$	2.408	63.4	1	$\bar{4}.592$	2.088	47.9
2	$\bar{4}.049$	2.869	82.8	2	$\bar{4}.269$	2.534	63.6
3	$\bar{5}.721$	3.314	108.4	3	$\bar{5}.940$	2.977	82.6
4	$\bar{5}.366$	3.758	133.1	4	$\bar{5}.590$	3.425	103.6
5	$\bar{6}.891$	4.201	152.1	5	$\bar{5}.229$	3.868	125.1

-33.5°C.

Series III				Series IV			
No.	log k	log V	Λ	No.	log k	log V	Λ
1	$\bar{4}.426$	2.542	92.9	1	$\bar{4}.679$	2.143	66.4
2	$\bar{4}.096$	2.984	117.5	2	$\bar{4}.357$	2.586	87.7
3	$\bar{5}.726$	3.427	142.3	3	$\bar{4}.009$	3.030	109.4
4	$\bar{5}.303$	3.870	149.1	4	$\bar{5}.640$	3.476	130.7

Series V

No.	log k	log V	Λ
1	$\bar{4}.514$	2.328	69.6
2	$\bar{4}.250$	2.773	105.5
3	$\bar{5}.884$	3.218	126.5

Table IV

Conductance of Potassium in Methylamine

-48.5°C.

Series I				Series II			
No.	log k	log v	Λ	No.	log k	log v	Λ
1	4.304	2.408	82.4	1	4.598	2.088	47.9
2	4.049	2.889	82.8	2	4.589	2.534	62.6
3	3.731	3.314	108.4	3	4.940	2.977	82.6
4	3.366	3.759	133.1	4	4.590	3.422	103.6
5	3.891	4.201	152.1	5	5.222	3.868	122.1

-32.5°C.

Series III				Series IV			
No.	log k	log v	Λ	No.	log k	log v	Λ
1	4.426	2.543	92.9	1	4.679	2.142	66.4
2	4.096	2.984	117.5	2	4.557	2.586	87.7
3	3.726	3.427	141.8	3	4.009	3.030	109.4
4	3.303	3.870	169.1	4	5.640	3.476	130.7

Series V

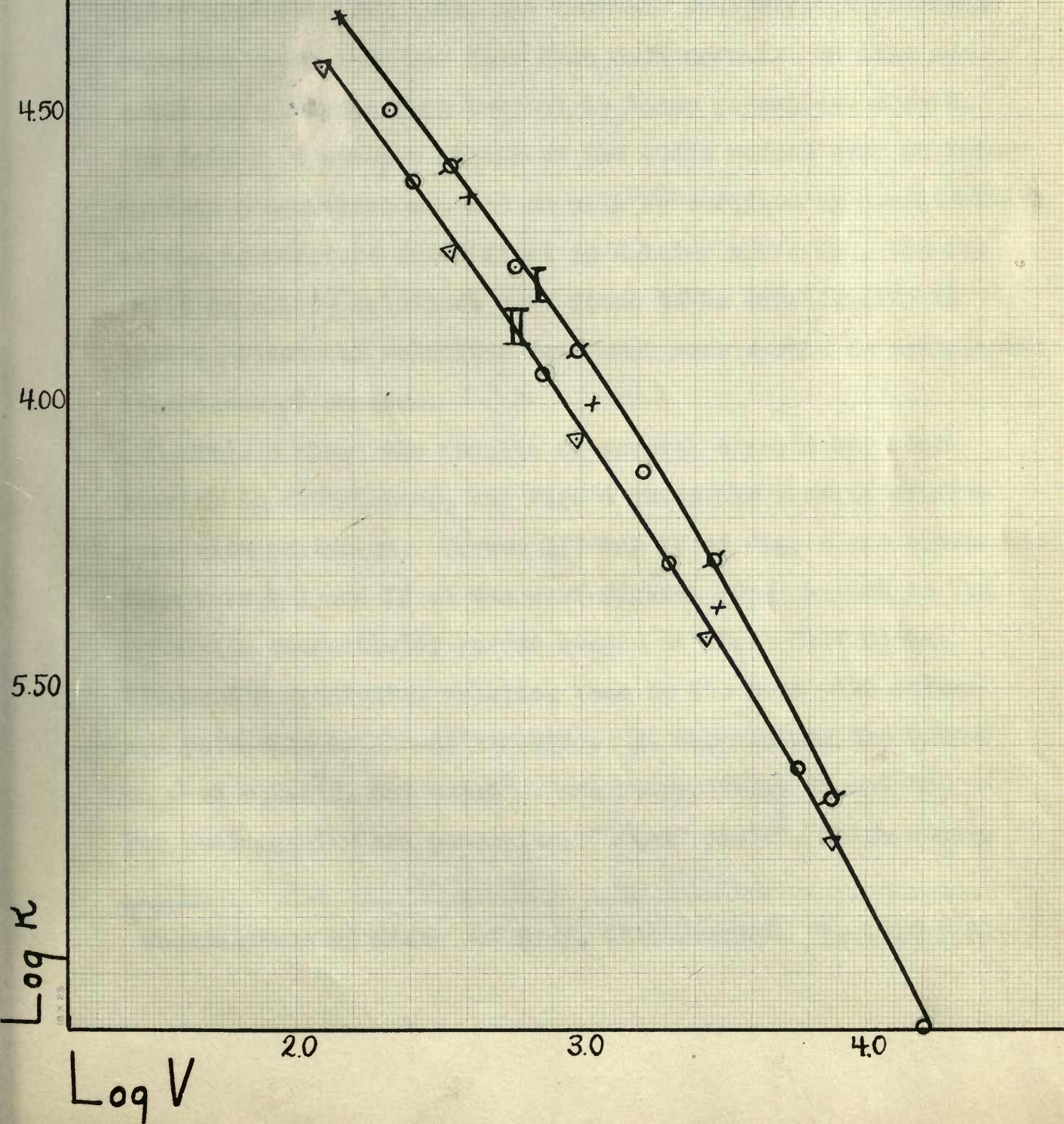
No.	log k	log v	Λ
1	4.514	2.828	69.6
2	4.250	3.272	102.5
3	3.884	3.718	126.6

Fig. 6

K in CH_3NH_2

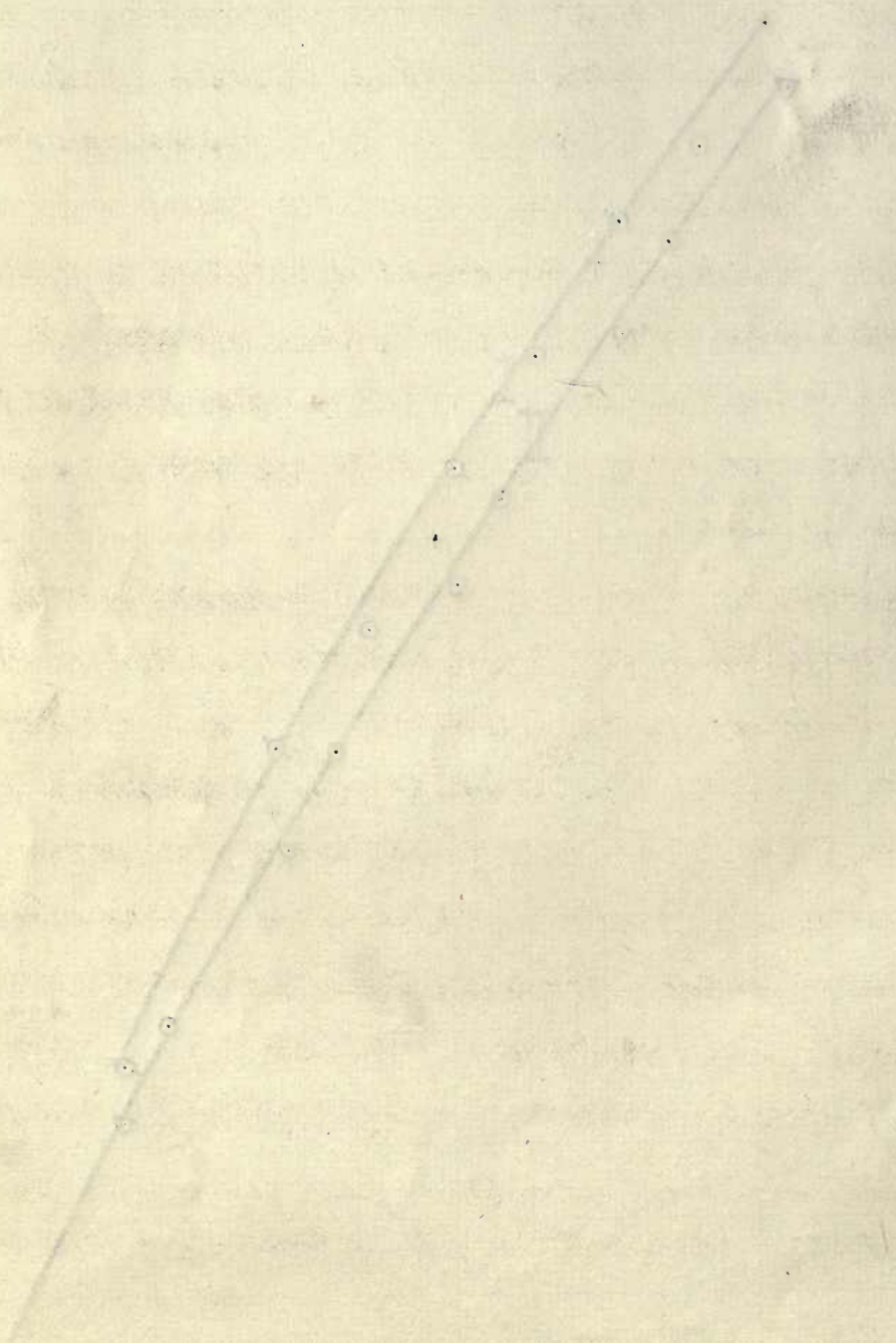
I - -33.5°C

II - -48.5°C



N. C. 1111

I-335-C II-382-C



In the case of potassium, two layers form at -33.5°C. , and the most concentrated blue layer is near 0.01 normal. Since the presence of a bronze layer makes a correct analysis of the blue layer impossible, only small quantities of potassium were introduced into the cell, and the most concentrated potassium solution determined was less than 0.01 normal. On this account the analyses were subject to large percentage errors. The fading of caesium solutions was quite marked even at intermediate concentrations, and as will be verified by consideration of the temperature coefficient in a later paragraph, the results in dilute solutions were found to be considerably in error. Potassium solutions were much more stable in methylamine than those of caesium.

Fig. 3 shows the results of several experiments with caesium in methylamine, and Fig. 4 shows the results of five runs with potassium. Curves III and IV of Fig. 3 are constructed from Curves I and II of the same figure. The minimum in the molecular conductivity curves occurs at about 0.07 normal (in more concentrated solution than is the case with sodium and potassium in liquid ammonia). At the minimum the values of Δ at -33.5°C. and -48.5°C. are respectively 51 and 33. For both caesium and potassium, " Δ_{∞} -k" plots¹, which assume

In the case of potassium, two layers form at -33.5°C., and the more concentrated blue layer is near 0.01 normal. Since the presence of a brown layer makes a correct analysis of the blue layer impossible, only small quantities of potassium are introduced into the cell, and the most concentrated potassium solution determined was less than 0.01 normal. On this account the analyses were subject to large percentage errors. The testing of cesium solutions was quite limited even at low molar concentrations, and as will be verified by consideration of the temperature coefficient in a later paragraph, the results in these solutions were found to be anomalously in error. Potassium solutions were much more stable in weight than those of cesium.

Fig. 3 shows the results of several experiments with cesium in methanol, and Fig. 4 shows the results of three runs with potassium. Curves III and IV of Fig. 3 are similar to curves I and II of the same figure. The minimum in the molar conductivity curves occurs at about 0.01 normal (in more concentrated solutions there is the case with sodium and potassium in liquid ammonia). At the minimum the values of Δ at -33.5°C. and -55.5°C. are respectively 31 and 33. For both cesium and potassium, Δ - κ plots, which assume

the validity of the mass law, were constructed, and led to the following values:

Temp.	Metal		k(mass law const.)
-33.5	K	159	21.4×10^{-4}
-48.5	K	144	11.2×10^{-4}
-33.5	Cs	188	19.4×10^{-4}
-48.5	Cs	174	13.9×10^{-4}

A single run was also made with caesium iodide¹ in methylamine, and the results of this experiment appear in Fig. 3, Curves V and VI. The position of these curves is substantially the same as that for potassium iodide in methylamine given by Franklin and Gibbs². "Δ.-k" plots for caesium iodide led to the following values:

Temp.		k(mass law const.)
-33.5	60.6	4.91×10^{-4}
-48.5	56.2	4.64×10^{-4}

Discussion of Results.

The true temperature coefficient in dilute solutions is independent of temperature. In Table V of his recent article

¹ Caesium chloride was found to be insoluble.

² Franklin and Gibbs, This Journal 29, 1391 (1907).

Gasoline chloride was found to be insoluble.

The true temperature coefficient in dilute solutions independent of temperature. In Table V of his recent article

Discussion of Results

the following values:

Temp.	(K ₂ SO ₄ law constant)
-35.5	4.81×10^{-4}
-42.5	4.84×10^{-4}

Franklin and Gibbs². Δ - Δ plots for cesium iodide 1st series as that for potassium iodide in methanol gave curves V and VI. The position of these curves is substantiated, and the results of this experiment appear in Fig. 5. A similar run was also made with cesium iodide in methanol.

Temp.	Model	(K ₂ SO ₄ law constant)
-35.5	X	41.4×10^{-4}
-42.5	X	11.2×10^{-4}
-35.5	O	12.4×10^{-4}
-42.5	O	12.9×10^{-4}

Following values:

the validity of the mass law, were connected, and led to

upon conductance in liquid ammonia¹, Kraus calculates values for $\Delta(1/R)/\Delta t(1/R_{33}) \times 100$, and this quantity increases rapidly with temperature. Evidence that the true temperature coefficient $d(\ln k)/dt$ is independent of temperature in dilute solutions is presented in Fig. 3. The three upper points are values for $\log R$ taken from Fig. 2 at 0.004 normal, and moved along the $\log R$ axis until the value at -33.5°C agrees with that of Kraus. The five lower points are Kraus's values for $\log R$ in "dilute solution" over a higher range of temperature. Weight is given to the points at the lower temperature where the fading was less. A straight line seems to be justified, since the aberration of the points at the higher temperatures is in the direction to be expected from fading.

At concentrations near the minimum there was evidence of a larger temperature coefficient at the higher temperature in the case of both sodium and potassium, but the effect was scarcely beyond the limit of experimental error, and could not be established with certainty.

In Table V is a summary of temperature coefficients calculated from the $\log k$ curves in the preceding figures. The values of $d(\log k)$ were taken directly from the plots. In the

¹
Loc. cit.

upon concentration in liquid ammonia, ΔH_{fus} calculated values for $\Delta H_{\text{fus}} / \Delta T \times 100$, and this quantity increases rapidly with temperature. Evidence that the true temperature coefficient $\Delta H_{\text{fus}} / \Delta T$ is independent of temperature in dilute solutions is presented in Fig. 2. The three upper points are values for log R taken from Fig. 2 at 0.001 molar and moved along the log R axis until the value of -35.5° agrees with that of ΔH_{fus} . The five lower points are known values for log R in "dilute solution" over a higher range of temperature. Weight is given to the points at the lower temperatures where the ratio was less. A straight line can be justified, since the deviation of the points at the higher temperatures is in the direction to be expected from testing.

At concentrations near the minimum there was evidence a larger temperature coefficient at the higher temperatures the case of both sodium and potassium, but the effect was scarcely beyond the limit of experimental error, and could be established with certainty.

In Table V is a summary of temperature coefficients calculated from the log R curves in the preceding figures. The values of $\Delta H_{\text{fus}} / \Delta T$ were taken directly from the plots. In

last column of Table V appear the values of $d(\ln k)/dt$ at one or more dilutions of the solute, and also an average value.

Table V
Summary of Temperature Coefficients

Log V	Temp. Range	Solute	Solvent	$d(\ln k)/dt$ $\times 10^3$	Average
1.4	-53 to -48	Na	NH_3	20.9	20.4
2.4	"	"	"	20.7	
1.4	-48 to -70	"	"	18.6	
2.4	"	"	"	21.6	
1.4	-33 to -48	K	NH_3	27.4	29.1
2.4	"	"	"	30.7	
2.0	-33 to -48	K	CH_3NH_2	20.6	19.8
3.0	"	"	"	19.0	
1.0	-53 to -48	Cs	CH_3NH_2	27.6	23.9
2.0	"	"	"	20.3	
3.0	"	"	"	9.2 (fading)	
1.3 - 3.0	"	CsI	CH_3NH_2	7.7	7.7

where ϕ is the viscosity, and m and n are constants, appears to be generally applicable. The value of m is usually very nearly unity. Hydrogen and hydroxyl ions are again excepted.

Kohlrausch and Holborn, Das Leitvermogen der Elektrolyte, (Teubner, Leipzig and Berlin, 1902)

Table V

Summary of Temperature Observations

Log V	Temp. Range	Points	Values	$\delta(\text{in } \mu)/\text{cm}$	Average
1.4	-25 to -45	12	20.2	{	20.4
2.4	"	"	20.1		
1.6	-45 to -70	"	19.6		
2.4	"	"	21.6		
1.6	-35 to -45	12	21.4	{	20.1
2.4	"	"	20.7		
2.0	-25 to -45	12	20.2	{	19.8
2.0	"	"	19.8		
1.0	-25 to -45	12	21.8	{	20.6
2.0	"	"	20.6		
2.0	"	"	2.2 (limit)	"	
1.2-2.0	"	12	21.2	21.2	21.2

last column of Table V appear the values of $d(\ln k)/dt$ at one or more dilutions for each solute, and also an average value for each solute.

The temperature coefficients are about the same in the two solvents. The rapid decline in the temperature coefficient of caesium in methylamine is ascribed to fading. For a 0.001 normal potassium solution, in which the fading was much slower, the temperature coefficient is still 19×10^{-3} , whereas at the same dilution in a caesium solution the value has fallen to 9×10^{-3} .

It has been pointed out by Kohlrausch¹ that the temperature coefficients of conductivity and viscosity in aqueous solutions of most salts are approximately the same. Hydrogen and hydroxyl ions are exceptions to this rule, the temperature coefficients of conductivity being abnormally low. Johnston² studied the relationship between viscosity and conductivity over a wide range of temperature in water and in non-aqueous solvents, and showed that the equation,

$$\Lambda = k\phi^m,$$

where ϕ is the fluidity, and m and k are constants, appears to be generally applicable. The value of m is usually very nearly unity. Hydrogen and hydroxyl ions are again exceptional.

¹

Kohlrausch und Holborn, Das Leitvermogen der Elektrolyte, p.127. (Teubner, Leipzig und Berlin, 1916)

²

This Journal, 31, 1010(1909).

Kohlrausch and Holborn, *Ann. Physik.* 27, 1 (1900).
(Weber, *Ann. Physik.* 18, 1 (1886).)

mostly unity. Hydrogen and hydrogen ions are again exceptions

to be generally applicable. The value of κ is usually very

where ϕ is the viscosity, and κ and κ' are constants, appears

$$\Delta = \kappa \phi^m$$

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normal potassium solution, in which the falling was much slower

of sodium in methylamine is ascribed to fading. For a 0.001

two solvents. The rapid decline in the temperature coefficients

The temperature coefficients are about the same in the

value for each solvent.

one or more divisions for each solvent, and also an average

last column of Table V appear the values of $\kappa(10^{-3})$ at

We may remark in passing that the low value of the temperature coefficient of conductivity of these ions might be accounted for if we assume the conductivity to be due in part to the liberation of a hydrogen or a hydroxyl ion at one end of a chain of water molecules, and a simultaneous binding of a hydrogen or a hydroxyl ion at the other end of the chain, without actual migration of the ions through the solution, as has been suggested by various authors¹ to account for the abnormally high conductance of these solutions. For, if we assume such chains of water molecules to become less stable at the higher temperatures, the diminution in this type of conduction would counteract the increase due to the diminishing viscosity of the solution, and thus give an abnormally low temperature coefficient. If we assume the rule of Kohlrausch to hold for methylamine, the temperature coefficient of the conductivity of all salts in this solvent should be approximately equal to that of caesium iodide. If this is true, the temperature coefficient of conductivity of the alkali metals in methylamine is abnormally high. This could be accounted for by a decreased solvation of the electrons with rise in temperature, - as was assumed by Gibson and Argo² as a possible explanation of the

¹ Lewis, *This Journal*, 34, 1642 (1912);
Latimer and Rodebush, *Ibid.*, 42, 1452 (1920).

² The conductivity rises very rapidly as the concentration is further increased. The minimum is approximately the same for
Loc. cit.

The present is passing that the low value of the temperature
 coefficient of conductivity of these ions might be accounted
 for if we assume the conductivity to be due in part to the
 liberation of a hydrogen or a hydroxyl ion at one end of a
 chain of water molecules, and a simultaneous binding of a
 hydrogen or a hydroxyl ion at the other end of the chain, with
 out actual migration of the ions through the solution, as has
 been suggested by various authors to account for the abnor-
 mally high conductance of these solutions. For, if we assume
 such chains of water molecules to become less stable at the
 higher temperatures, the liberation in this type of conduction
 would counteract the increase due to the diminishing viscosity
 of the solution, and then give an abnormally low temperature
 coefficient. If we assume the rate of recombination to hold for
 determining the temperature coefficient of the conductivity
 of all salts in this solvent should be experimentally equal to
 that of sodium hydroxide. If this is true, the temperature coef-
 ficient of conductivity of the alkali metals in methanol is
 abnormally high. This result is accounted for by a decreased
 solvation of the anions with rise in temperature, - as was
 suggested by Gibson and Lipp² as a possible explanation of the

¹ Lewis, THIS JOURNAL, 36, 1662 (1912);
 Bateman and Kobernick, THIS JOURNAL, 42, 1422 (1918).

diminution in the coefficient of absorption of these solutions with increasing temperature.

In order to account for the deviation from Beer's Law for the shorter wave-lengths in solutions of the alkali metals in methylamine, Gibson and Argo assumed the absorption at these wave-lengths to be partly due to unionized metal. Since the solutions in ammonia do not show this deviation from Beer's Law, they assumed the ionization in ammonia to be more complete than in methylamine. The dissociation constant for the metals in ammonia is greater than that in methylamine, but the difference is hardly sufficient to account for the deviations which they observed. The deviation from Beer's Law may nevertheless be due to unionized metal, for the absorption due to unionized metal in ammonia may not be in the visible spectrum. This point could not be decided without a knowledge of the absorption curve in ammonia at other wave-lengths.

We have already mentioned that the conductivity curves of the metals in ammonia and in methylamine are of the same general type, the conductivity diminishing at first according to the mass law in dilute solutions, becoming greater than would be predicted from the mass law in more concentrated solutions, until a minimum in the conductivity is reached, after which the conductivity rises very rapidly as the concentration is further increased. The minimum is approximately the same for

variation in the coefficient of absorption of these solutions
with increasing temperature.

In order to account for the deviation from Beer's law the
the shorter wave-lengths in solution at the same molar
in methylene blue and also account for the absorption at these
wave-lengths to be partly due to un-ionized molecules. Since the
solution is assumed to be not more than this deviation from Beer's law
they account for the variation in molar absorptivity to be more complex than
in methylene blue. The absorption constant for the molar in
molar is greater than that in methylene blue, but the difference
is hardly sufficient to account for the variations which they
observe. The deviation from Beer's law may nevertheless be
due to un-ionized molecules, for the absorption due to un-ionized molecules
in molar may not be in the visible spectrum. This point can
not be settled without a knowledge of the absorption curves in
molar at other wave-lengths.

We have already mentioned that the conductivity curves of
the curve in molar and in methylene blue are of the same general
type, the conductivity increasing at first according to the
molar law in dilute solutions, becoming greater than would be
predicted from the molar law in more concentrated solutions,
until a minimum in the conductivity is reached, after which
the conductivity rises very rapidly as the concentration is
further increased. The minimum is approximately the same for

all the metals in any one solvent, but occurs at a somewhat lower concentration in ammonia than in methylamine. If we assume the increase in conductivity to the higher concentrations to be due to the influence of free ions in the solution, which cause a diminution in the electrical forces, - for much the same reason that an increase in the dielectric constant would cause a diminution in these forces, - we should expect a deviation from the mass law to occur at lower concentrations in a solution which is highly ionized than in one which is less so. We have seen that the metals are more highly ionized in ammonia than in methylamine; hence the solutions in ammonia, other things being equal, should show a minimum at lower concentrations than those in methylamine, as is actually observed. The extreme rapidity of the increase in conductivity at concentrations beyond the minimum points to a rapid diminution in the solvation of the electrons as the concentration is increased. This would seem to indicate that the force binding the electron to the solvent is electrical in character, and is diminished in concentrated solutions for the same reason that the ionization of the metal is increased, - namely owing to a diminution in the electrical forces due to the presence of free ions in the solution.

A certain amount of support for the assumption that the

all the metals in any one solvent, but occurs at a somewhat lower concentration in ammonia than in methyamine. It we assume the increase in conductivity to the higher concentrations to be due to the influence of free ions in the solution, which causes a diminution in the electrolytic forces, - for when the same reason that an increase in the electrolytic constant would cause a diminution in these forces, - we should expect a deviation from the same law to occur at lower concentrations in a solution which is highly ionized than in one which is less so. We have seen that the metals are more highly ionized in ammonia than in methyamine; hence the solutions in ammonia, other things being equal, should show a minimum at lower concentrations than those in methyamine, as is actually observed. The extreme rapidity of the increase in conductivity at some fraction beyond the minimum points to a rapid diminution in the ionization of the electrolyte as the concentration is increased. This would seem to indicate that the force binding the electrolyte to the solvent is electrical in character, and is diminished in concentrated solutions for the same reason that the ionization of the metal is increased, - namely owing to a diminution in the electrolytic forces due to the presence of free ions in the solution.

A certain amount of support for the assumption that the

attraction between the electron and the solvent is electrical in character is given by the fact that the absorption maximum in methylamine occurs at a shorter wave-length than in ammonia. In the latter solvent the measurements of Gibson and Argo¹ appear to indicate an absorption maximum in the infra-red. The dielectric constant of ammonia is greater than that of methylamine and we should therefore expect the electron to be less firmly bound in ammonia than in methylamine if the binding force is electrical in character. Determinations of the absorption maxima of lithium in ethylamine and propylamine, and a determination of the dielectric constants of these solvents should throw light on this question.

function between the electron and the electron is electric
character is given by the fact that the absorption curve
corresponding to a shorter wave-length than in some
the latter curve the measurement of electron and size
near to indicate an absorption maximum in the infra-red.
electric constant of ammonia is greater than that of
hydrogen and we might therefore expect the electron to
be strongly bound in ammonia than in hydrogen. The dis-
tance in electron is character. Determination of the
electron number of lithium in ethylene and propylene,
a determination of the electric constant of these
the electric theory light on this question.



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